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TERNARY AND QUATERNARY OXIDES OF Bi, Sr and Cu

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Before the discovery[1] of superconductivity in an oxide of Bi, Sr, and Cu, the system Bi-Sr-Cu-O had not been studied, although several solid phases had been identified in the two-component regions of the ternary system Bi_2O_3-SrO-CuO. The oxides Sr_2CuO_3, $SrCu_2O_2$, $SrCuO_2$, and Bi_2CuO_4 were then well known and characterized[2-10], and the phase diagram of the binary system Bi_2O_3-SrO had been established[11] in the temperature range 620-1000 °C. Besides nine solid solutions of compositions $Bi_{2-2x}Sr_xO_{3-2x}$ and different symmetries[12-15], this diagram includes three definite compounds of stoichiometries Bi_2SrO_4, $Bi_2Sr_2O_5$, and $Bi_2Sr_3O_6$ (x = 0.50, 0.67 and 0.75 respectively), only the second of which with known unit-cell of orthorhombic symmetry, dimensions (Å) **a** = 14.293(2), **b** = 7.651(2), **c** = 6.172(1), and Z = 4.

The first superconducting oxide in the system Bi-Sr-Cu-O was initially formulated[1] as $Bi_2Sr_2Cu_2O_{7+x}$, with an orthorhombic unit-cell of parameters (Å) **a** = 5.32, **b** = 26.6, **c** = 48.8. The superconducting transition at about 7 K was soon confirmed[16] for this oxide, that was described as showing a pseudo-tetragonal unit-cell, **a** = 5.38 Å, **c** = 24.6 Å, and signs of a weak superstructure with 5-fold periodicity along the **b**-axis. In a preliminary study some of the authors of the present paper formulated[17] the same oxide with half the copper content, $Bi_2Sr_2CuO_{6+x}$, and indexed its reflections assuming an orthorhombic unit-cell of dimensions (Å) **a** = 5.390(2), **b** = 26.973(8), **c** = 24.69(4). Subsequent studies[18-25] by diffraction techniques have confirmed the composition 2:2:1, proposing for this oxide the substructures included in table I.

Table I. Crystal structures proposed for superconducting $Bi_2Sr_2CuO_{6+x}$

Symmetry	S.G.	a/Å	b/Å	c/Å	β (°)	Z	Ref.
T	-	5.381(1)	-	24.65(1)	-	-	18
T	I4/mmm	3.8097(4)	-	24.607(3)	-	2	19
O	Amaa	5.392	5.394	24.537	-	4	20
O	-	10.8	53	24	-	-	21
T	I4/mmm	3.801(3)	-	24.61(9)	-	2	22
O	Amaa	5.362(3)	5.374(1)	24.622(6)	-	-	23
T	-	5.4	-	24.6	-	-	24
M	C2	26.856	5.380	26.908	113.55	4	25
M	-	5.4	26	28	116	-	26

T: tetragonal O: orthorhombic M: monoclinic

The real structure is a modulated superstructure:for instance, the tetragonal substructure **a** = 5.4 Å, **c** = 24.6 Å of table I includes three kinds of long period superstructures that were observed[24] by electron diffraction: 1) base-centered monoclinic with parameters (Å): **a** = 5.4, **b** = 27, **c** = 26.9, α = 66.3° ; 2) simple monoclinic with **a** = 5.4, **b** = 27, **c** = 12.6, α = 77.6°; and 3) base-centered orthorhombic, with 5.4x22.6x24.6 Å^3. 'Single' crystals of $Bi_2Sr_2CuO_{6+x}$ often contain syntactic intergrowths of more than one phase, which are related to stacking faults along the **c** axis. These intergrowths are so abundant, that 'single' crystals are not neccesarily homogeneous with regard to either structure or composition.

Besides the phase with molar ratios Bi:Sr:Cu = 2:2:1, three quaternary oxides are known with ratios 4:8:5, 17:16:7, and 2:3:2. The crystal structure of $Bi_4Sr_8Cu_5O_{19+x}$ has been established[27]: the unit-cell is orthorhombic, S.G. Fmmm, with parameters (Å) **a** = 5.372(2), **b** = 33.907(6), **c** = 23.966(4). The unit-cell parameters (Å) of the other two oxides have been determined[28] in polycrystalline samples. Both are orthorhombic, with **a** = 5.425, **b** = 23.254, **c** = 24.427 for the phase 17:16:7, and **a** = 4.888, **b** = 5.396, **c** = 24.804 for the oxide 2:3:2.

The authors of the present paper have been able to characterize a new family of oxygen-deficient perovskites, $Sr(Sr_{0.5}\ Bi_{0.5-x}\ Cu_x)\ O_{2.75-1.5x}$ ($0.2 > x > 0$), after identifying by X-ray diffraction the phases present in the products of thermal treatments of about 150 mixtures of analytical grade Bi_2O_3, $Sr(OH)_2.8H_2O$ and CuO at different molar ratios. The basic compound, $Sr(Sr_{0.5}Bi_{0.5})O_{2.75}$, was prepared from stoichiometric mixtures of the reagents, that were ground in an agate mortar, and then fired for 5 hours at 700 °C in alumina crucibles. The product was reground, fired again for 5 hours at 800 °C, reground, and heated for 5 hours at 900 °C. The mass changes, that were followed by weighing before and after each operation, showed that practically the whole Bi (III) oxidized to Bi (V) in the course of the thermal treatments.

The X-ray powder diffraction pattern for $Sr(Sr_{0.5}\ Bi_{0.5})O_{2.75}$ shows the reflexions of a cubic perovskite, **a** = 2**a**$_o$ = 8.493(7) Å, with 1:1 order at the B-cations sublattice. This basic compound, which appears as not too crystalline, admits to substitute some Cu for Bi.

$Sr(Sr_{0.5}Bi_{0.3}Cu_{0.2})O_{2.45}$ was prepared from stoichiometric mixtures of the reagents, which were heated as indicated for the basic compound. Its unit-cell parameter, **a** = 8.465(14) Å, is slightly smaller than that for $Sr(Sr_{0.5}Bi_{0.5})O_{2.75}$. This could be expected considering the different size[29] of both cations, 0.76 Å for Bi^{5+} and 0.73 Å for Cu^{2+}, as well as the smaller oxygen content of the Cu compound.

Finally, the authors will present X-ray diffraction data for some other oxides of Bi and Sr, as well as for various quaternary oxides, among them a novel oxide of Bi, Sr, and Cu.

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